Ordered Phase of the Dipolar Spin Ice under [110]-Magnetic Fields

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We find that the true ground state of the dipolar spin ice system under [110]-magnetic fields is the "$Q = X$" structure, which is consistent with both experiments and Monte Carlo simulations. We then perform a Monte Carlo simulation to confirm that there exists a first order phase transition under the [110]-field. In particular this result indicates the existence of the first order phase transition to the "$Q = X$" phase in the field above 0.35 T for $Dy_2Ti_2O_7$. We also show the magnetic field-temperature phase diagram to summarize the ordered states of this system.

Keywords: spin ice, Ising chain, Monte Carlo simulation, pyrochlore lattice, $Dy_2Ti_2O_7$

Spin ice (SI) materials such as $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ have been attracting much interest as one of the ideal model materials of geometrically frustrated systems [1, 2]. In the SI materials, the magnetic moments occupy a three dimensional network of corner sharing tetrahedra with cubic symmetry called the pyrochlore lattice (FIG.1). Each magnetic moment is forced to point toward either of two tetrahedron centers by the strong crystal field along the local $\langle 111 \rangle$ axes [3, 4]. Then ferromagnetic nearest neighbor interactions lead to a geometrical frustration among four spins in a tetrahedron and the local ground states in each tetrahedron are six-fold degenerated. These local ground states are determined by the rule that two spins point inward and two spins outward. This "2-in & 2-out" rule is called the ice rule from the analogy to the ice I_h [1]. Under the ice rule, a number of low-lying states exist in the system and there remains a residual entropy almost same as the Pauling value [5, 6, 7].

It has been suggested that the large dipole interaction is responsible for the spin ice behavior in the SI materials [8]. In the SI model with long range dipole interaction (the dipolar spin ice, DSI), it would be expected that the degeneracy of the ground state is removed by the long range nature of the dipole interaction and a long range order exists at low temperatures. Hertog *et al.* performed single spin flip Monte Carlo (MC) simulations of the DSI at zero field by using Ewald method and concluded that there is no long range order and there remains certain residual entropy close to the Pauling value [8]. Melko *et al.*, however, found the phase transition to the long range ordered $\boldsymbol{q}_{\rm ord} = (0, 0, 2\pi/a)$ phase, where a is the size of conventional cubic unit cell, by MC simulations employing the loop algorithm which improves the dynamics at low temperature. This $\boldsymbol{q}_{\rm ord}$ order was identified as the true ordered ground state at zero field by the Fourier transformation of the interaction [10].

Recently, the SI materials under magnetic fields along the [110]-direction have been studied by means of single crystal experiments [1, 11, 13]. Fennel *et al.* performed neutron diffraction experiments of $Dy_2Ti_2O_7$ under the [110]-magnetic fields with fixed low temperature $\sim$ 70 mK, which shows magnetic Bragg peaks at the $Q = 0$ points and diffuse scattering at the $Q = X$ points [11]. From their scattering patterns, they found the coexistence of long-range ferromagnetic order on the field coupled spin chains (called α-chains by Hiroi *et al.* [13], FIG.1) and short-range antiferromagnetic order on the field independent spin chains (β-chains). They suggested that the true ground state is the $Q = X$ structure as shown in FIG.1 [1, 11], although they could not find a clear evidence for such ordered state. A similar result was found in neutron diffraction experiments of $Ho_2Ti_2O_7$ by Harris *et al* [1]. On the other hand, Hiroi *et al.* performed specific heat measurements of $Dy_2Ti_2O_7$ in the [110]-magnetic fields. They found a relatively sharp peak at 1.1 K (below the broad peak associated with SI

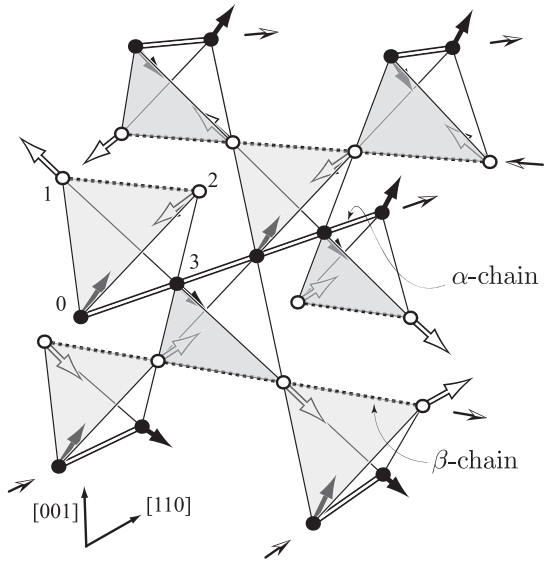

FIG. 1: A schematic plot of the pyrochlore lattice and $Q = X$ configuration. The magnetic ions are located at each vertex of the tetrahedra. The numbers in the figure indicate the Ising axis indices $\nu = 0, 1, 2, 3$. Under the [110]-fields, the system is divided into two sets of spin chains, α-chain (double line) and β-chain (dotted line) . The [110]-field affects spins only on the α-chains.

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freezing at low fields) in the field $H \gtrsim 0.4$ T. They suggested that this peak comes from the freezing of β-chains without long range order. They also argued the frustration between β-chains and threw doubt on the $Q = X$ structure as the true ground state [13]. In the theoretical point of view, Melko *et al.* performed MC simulations to observe a first order phase transition to the $Q = X$ structure [12]. Thus the $Q = X$ structure is still controversial.

In the [110]-fields, there remains ground state degeneracy on the β-chains as far as only the nearest neighbor interaction is taken into account. We expect that this degeneracy is removed by the dipole interaction. In this paper, we give a proof that the $Q = X$ structure is the true ground state configuration under the [110]-fields. We then perform single spin flip MC simulations to show that the relatively sharp specific heat peak originates from the first order phase transition to the $Q = X$ phase and to present the temperature-field phase diagram.

In the spin ice compound, each spin $\boldsymbol{s}_i$ is forced to align along its easy axis $\boldsymbol{n}_i$ due to the strong crystal field, so that it is expressed with an Ising variable $\sigma_i(= \pm 1)$ as $\boldsymbol{s}_i = \sigma_i \boldsymbol{n}_i$, where $\boldsymbol{n}_i$ is one of the four distinct Ising axes $\boldsymbol{n}_\nu$; $\nu = 0, 1, 2, 3$ corresponding to each site on the basic tetrahedron (FIG.1). Then the Hamiltonian of the Ising DSI system with N spins under an uniform external field $\boldsymbol{H}$ is given as

$$\begin{aligned}
&\mathcal{H}(\sigma_1, \sigma_2, \cdots, \sigma_N) \\
&= -p_{\rm eff}\mu_{\rm B} \sum_i (\boldsymbol{H} \cdot \boldsymbol{n}_i)\sigma_i + (J_{\rm nn} + D_{\rm nn}) \sum_{\langle ij \rangle}^{\rm nn} \sigma_i \sigma_j \\
&+ \frac{3D_{\rm nn} {r_{\rm nn}}^3}{5} \sum_{\langle ij \rangle}^{\rm long} \frac{|\boldsymbol{r}_{ij}|^2 (\boldsymbol{n}_i \cdot \boldsymbol{n}_j) - 3(\boldsymbol{r}_{ij} \cdot \boldsymbol{n}_i)(\boldsymbol{r}_{ij} \cdot \boldsymbol{n}_j)}{|\boldsymbol{r}_{ij}|^5} \sigma_i \sigma_j \,,
\end{aligned} \tag{1}$$

where the second and the last terms represent the nearest neighbor interactions (both exchange $J_{\rm nn}$ and dipole $D_{\rm nn}$) and the long range part of the dipole interactions, respectively. By using the size of unit cell a, the nearest neighbor distance $r_{\rm nn}$ is written as $r_{\rm nn} = a/\sqrt{8}$. In this paper we use material parameters of $Dy_2Ti_2O_7$: $J_{\rm nn} = -1.24$ K, $D_{\rm nn} = 2.35$ K and $p_{\rm eff}\mu_{\rm B} = 10.6\mu_{\rm B} = 7.09$ $\rm KT^{-1}$ [8].

First, we consider the effect of magnetic field along the [110]-direction without the long range interaction term. In the [110]-fields, the pyrochlore lattice is divided into two sets of Ising spin chains named as α and β-chains, as illustrated in FIG.1 [11, 13]. Spins on the $\nu = 0, 3$ sites compose α-chains and ones on the $\nu = 1, 2$ sites β-chains. The [110]-magnetic fields affect spins only on the α-chains and tend to align them ferromagnetically. Being free from the [110]-magnetic fields, spins on a β-chain also align ferromagnetically due to the ice rule when the α-chains are ordered ferromagnetically. It should be noted that each ferromagnetic β-chain has two possible states and the ground states are 2^{N_β}-fold degenerated, where $N_\beta \sim N^{2/3}$ is the number of the β-chains. At the ground state, the inter-chain configuration of α-chains is ferromagnetic (F) while the one of β-chains is paramagnetic (P). Here we introduce abbreviated notations for inter-chain configurations of the α/β-chains for convenience. The inter-chain configuration of the α-chains is abbreviated as α-AF if they are ordered antiferromagnetically (AF). In this notation, the ground state configuration mentioned above is expressed as "α-F & β-P". Thus there is no phase transition to the long range ordered phase without the long range interaction.

Now, we consider the effect of the long range interaction. At zero field, the long range interaction removes the macroscopic degeneracy of the ground states and the $\boldsymbol{q}_{\rm ord} = (0, 0, 2\pi/a)$ configurations become the true ground states [9, 10]. In terms of the inter-chain configuration of the α/β-chains, these ground states are expressed as "α-AF & β-AF". In order to show that the $Q = X$ structure, which is expressed as "α-F & β-AF" (see FIG.1), is the true ground state under [110]-magnetic fields, we only consider F and AF inter-chain alignments for the α/β-chains. By means of the Ewald summation techniques, we calculated the interaction energy of the four configurations for $\boldsymbol{H} = \boldsymbol{0}$ and obtained

$$\begin{aligned}
&\frac{1}{N}E_0^{\alpha\text{-AF},\beta\text{-AF}} = -1.5060 \text{ K}\,, \ \frac{1}{N}E_0^{\alpha\text{-F},\beta\text{-F}} = -0.6816 \text{ K}\,, \\
&\frac{1}{N}E_0^{\alpha\text{-F},\beta\text{-AF}} = \frac{1}{N}E_0^{\alpha\text{-AF},\beta\text{-F}} = -1.0938 \text{ K}\,.
\end{aligned} \tag{2}$$

Note that the two energy differences $E_0^{\alpha\text{-F},\beta\text{-AF}} - E_0^{\alpha\text{-AF},\beta\text{-AF}}$ and $E_0^{\alpha\text{-F},\beta\text{-F}} - E_0^{\alpha\text{-F},\beta\text{-AF}}$ are both 0.4122 K per spin. This result implies that there is no interaction between the α and β-chains as far as F and AF inter-chain alignment are concerned. Indeed this statement is true since the internal fields acting on the β-chains from the α-F/AF chains are canceled out each other due to the symmetry of the pyrochlore lattice structure. Since "α-AF & β-AF" is the ground state at zero field, we can say that each set of ferromagnetic Ising spin chains tends to align anti-ferromagnetically. In the [110]-field, the energy of the "α-F & β-AF" configuration comes down while the energy of the "α-AF & β-AF" configuration does not change. So there is a ground state transition field $H_{\rm c}$, at which the following equation holds:

$$\frac{1}{N}E_0^{\alpha\text{-AF},\beta\text{-AF}} = \frac{1}{N}E_0^{\alpha\text{-F},\beta\text{-AF}} - \frac{1}{\sqrt{6}}\, p_{\rm eff}\mu_{\rm B}H_{\rm c}\,. \tag{3}$$

Using these values given in eq.(2), we obtain the transition point $H_{\rm c} = 0.142$ T. Thus we conclude that the "α-F & β-AF" ($Q = X$) configuration is the true ground state in the field $H > H_c$.

Next we perform single spin flip MC simulations to show that there exists phase transition to the "α-F & β-AF" phase. Our simulations were carried out on system size up to 5488 spins (cubic unit cell length $L = 7$) with a slow cooling process. The simulation lengths were $\sim 10^5$ MC steps per spin at each temperature. In FIG.

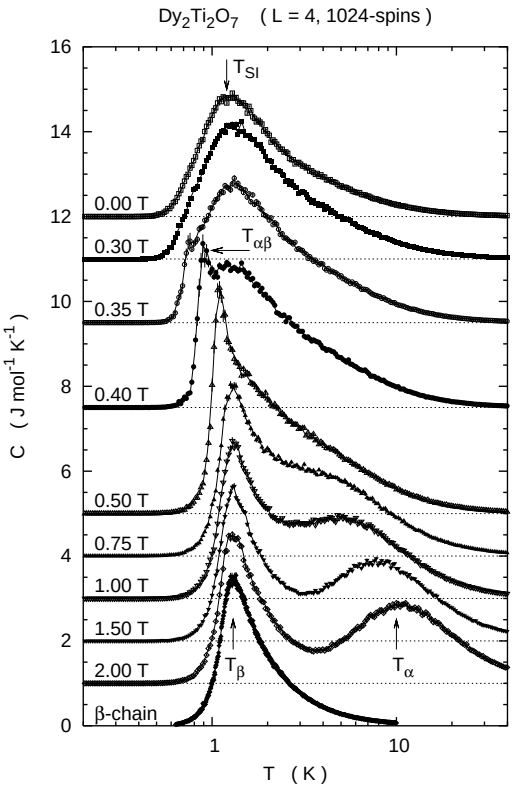

FIG. 2: Temperature dependence of the specific heat for various magnetic fields along the [110]-direction. Each data set has been shifted for clarity. The dotted line indicates the zero level for each set. Four characteristic peaks at $T_{\rm SI}$, $T_{\alpha\beta}$, T_α, T_β are also indicated (see text).

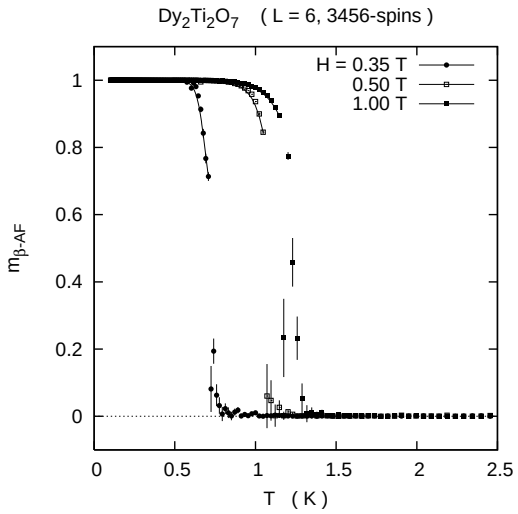

FIG. 3: Temperature dependence of the β-AF order parameter for [110]-magnetic fields $H = 0.35$ T, 0.50 T and 1.00 T.

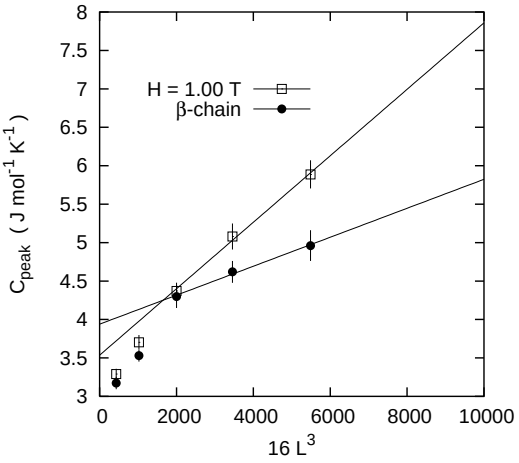

FIG. 4: Finite size scaling of the peak height of the specific heat as a function of system size $N = 16L^3$ for L=3, 4, 5, 6, 7.

2 we show our MC results for the temperature dependence of the specific heat for system size $L = 4$ under various magnetic fields H. At zero field a broad peak corresponding to the freezing into the SI state is found around $T_{\rm SI} \simeq 1.2$ K, in good agreement with the previous results [8]. As the magnetic field increases, the peak at $T_{\rm SI}$ grows up to $H = 0.30$ T, and then at $H = 0.35$ T a small anomalous peak appears at $T_{\alpha\beta}$ on the low temperature side of $T_{\rm SI}$, and this anomalous peak moves to the high temperature side. At $H = 0.50$T, the peak at $T_{\alpha\beta}$ merges with the broad peak at $T_{\rm SI}$ and there appears a very sharp peak, and then this peak is broken into two peaks at T_α and T_β. The peak at T_α is broad and shifts to the high temperature side with increasing field. On the other hand, the peak at T_β is sharp and almost independent of the field. From their field dependences, the peaks at T_α and at T_β must come from the α and β-chains, respectively. To extract the contribution of the β-chains, we performed a MC simulation of the system only with spins on the β-chains. This system equals to the DSI at the high-field limit since the spins on the β-chains feel no internal field from the α-F chains. The temperature dependence is also shown in the FIG. 2 and we see a sharp peak near $T_\beta \sim 1.3$ K. This sharp peak corresponds to the peak at T_β in large but finite magnetic fields as expected. These temperature and field dependences of the specific heat are also seen in the experiments by Hiroi *et al* [13].

In order to consider what happens at each peak more precisely, we observe order parameters corresponding to the inter-chain orders. For example, the order parameter for the β-AF order $m_{\beta\text{-AF}}$ is the $\boldsymbol{q}_{\rm ord} = (0,\, 0,\, 2\pi/a)$ staggered magnetization of the β-chains. In FIG.3 we show the temperature dependence of $m_{\beta\text{-AF}}$ for system size $L = 6$. We can see the β-AF order below $T_{\alpha\beta}$ and T_β, and discontinuity of the order parameter $m_{\beta\text{-AF}}$ at these temperatures. We also find from the observation of $m_{\alpha\text{-F}}$ that the field sensitive broad peak at T_α comes from the

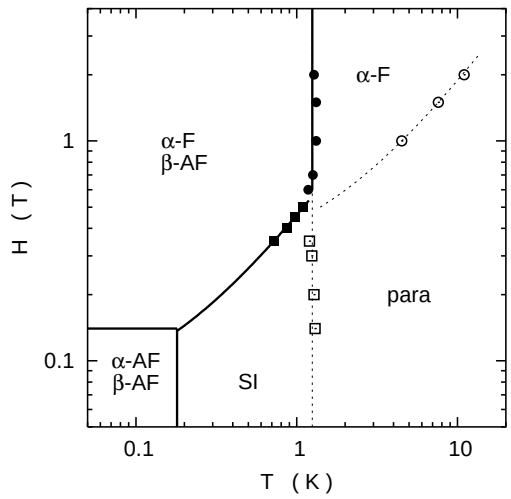

FIG. 5: Magnetic field-temperature phase diagram for $\boldsymbol{H} \parallel [110]$. The open squares, closed squares, open circles and closed circles indicate the characteristic peaks $T_{\rm SI}$, $T_{\alpha\beta}$, T_α and T_β, respectively. The solid line shows the first order phase transition and the dotted the crossover.

α-F freezing. Therefore the low temperature anomalous peak at $T_{\alpha\beta}$ and the field independent peak at T_β are due to the first order phase transition to the "α-F & β-AF" ordered phase. We also carried out a finite size scaling of the peak height $C_{\rm peak}$ for the magnetic field $H = 1.00$T and for the β-chain system (FIG.4). The scaling data shows that $C_{\rm peak}$ is proportional to the system size L^3 for large systems ($L \geq 5$). These results prove that the phase transition is indeed of the first order.

Finally we summarize our results from the ground state analysis and the MC simulation as a phase diagram in FIG.5. The data points in the diagram indicate the specific heat peak temperatures $T_{\rm SI}$, $T_{\alpha\beta}$, T_α, T_β in the MC results with single-spin-flip slow cooling process (FIG.2). The solid line in the diagram corresponds to the first order phase transition. Note that the straight lines shown in the low temperature and in the weak field region are expectation ones from the ground state transition field $H_{\rm c} = 0.142$ T and the zero field MC results [9]. In the cooling process at high field region, spins on the α-chains are almost fixed by the [110]-magnetic field below T_α, while the spins on the β-chains still take random configurations ("α-F" phase). Then at T_β the spins on the β-chains form the β-AF order and the phase transition to the "α-F & β-AF" configuration takes place due to the ice rule and the long range dipole interaction. In the weak field region $H < 0.30$ T, the phase transition has not been observed in our single spin flip MC simulation.

In conclusion, we have studied the effect of the dipole interaction on the DSI system under the [110]-magnetic fields through the ground state analysis and the single spin flip MC study. We have found that the "α-F & β-AF" ($Q = X$) configuration is the true ground state in the strong field region $H > H_{\rm c} = 0.142$ T and the first order phase transition from the "α-F" phase to the "α-F & β-AF" phase occurs. We have presented the [110]-field-temperature phase diagram. Melko *et al.* applied the loop algorithm and the multicanonical MC method in order to avoid the freezing at low temperature in the first order phase transition [9, 12]. Such techniques will clarify the detail of phase boundary in the low temperature and the weak field region, and are now under progress.

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